

CRYSTALLIZATION BEHAVIOR AND MORPHOLOGY OF ONE-STEP REACTION COMPATIBILIZED MICROFIBRILLAR REINFORCED ISOTACTIC POLYPROPYLENE/POLY(ETHYLENE TEREPHTHALATE) (*i*PP/PET) BLENDS*

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Abstract One-step reaction compatibilized microfibrillar reinforced *i*PP/PET blends (CMRB) were successfully prepared through a “slit extrusion-hot stretching-quenching” process. Crystallization behavior and morphology of CMRB were systematically investigated. Scanning electronic microscopy (SEM) observations showed blurry interface of compatibilized common blend (CCB). The crystallization behavior of neat *i*PP, CCB, microfibrillar reinforced *i*PP/PET blend (MRB) and CMRB was investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The increase of crystallization temperature and crystallization rate during nonisothermal crystallization process indicated both PET particles and microfibrils could serve as nucleating agents and PET microfibrils exhibited higher heterogeneous nucleation ability, which were also vividly revealed by results of POM. Compared with MRB sample, CMRB sample has lower crystallization temperature due to existence of PET microfibrils with smaller aspect ratio and wider distribution. In addition, since *in situ* compatibilizer tends to stay in the interphase, it could also hinder the diffusion of *i*PP molecules to the surface of PET phase, leading to decrease of crystallization rate. Two-dimensional wide-angle X-ray diffraction (2D-WAXD) was performed to characterize the crystalline structure of the samples by injection molding, and it was found that well-developed PET microfibrils contained in MRB sample promoted formation of β -phase of *i*PP.

Keywords: Isotactic polypropylene; Poly(ethylene terephthalate); *In situ* compatibilization; Microfibrillar reinforced blends; Crystallization behavior.

INTRODUCTION

Isotactic polypropylene (*i*PP) is one of the most widely used thermoplastic polymers and its consumption in industry grows quickly over the past years, which is attributed to its superior comprehensive properties, *viz.* low cost, easy processing, moderate mechanical properties, *etc.*^[1] These properties meet most demands very well such as daily supplies (food container, bag, and so on), however, its mechanical properties (modulus, tensile strength, impact strength, *etc.*) are not suitable for several engineering applications such as automobile industry^[2]. To solve these problems, blending *i*PP with other polymers, especially engineering polymers, such as poly(ethylene terephthalate) (PET), polycarbonate (PC) and polyamide (PA), is a convenient strategy to reinforce *i*PP and achieve high performance^[3–5]. For polymer blends, the morphology of dispersed phase plays an important role in their properties, for example, well-dispersed spheres or ellipsoids in matrix increase impact strength of materials, a sheet-like dispersed morphology owns an ability to enhance barrier properties of a film,

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and microfibrils can significantly improve tensile properties of polymer blends^[6–8]. Therefore, it is of great importance to understand the mechanism of formation of dispersed phase morphology during processing in order to take better control of processing conditions and finally make materials meet different needs. Based on these phenomena, we formerly prepared iPP/PET blends with controlled morphology of dispersed phase^[9], named microfibrillar reinforced PET/iPP blend, *via* the “slit-die-extrusion, hot-stretching, quenching” process, and the PET microfibrils were generated successfully during processing. Moreover, a significant reinforcing effect of the *in situ* formed microfibrils on the matrix was achieved.

Essentially, iPP and PET are thermodynamically immiscible and technologically incompatible. Therefore, they need to be compatibilized in order to improve adhesion between the two phases, although the reinforcement effect also occurs in microfibrillar reinforced iPP/PET blends due to pressure acting on the PET microfibrils caused by the difference between thermal shrinkage of PET and iPP from processing temperature to room temperature^[10, 11]. It is well known that a desired and stabilized state of an immiscible polymer blend with sufficiently strong interfacial adhesion can be obtained by addition of an appropriate interfacial agent (compatibilizer), such as some block or graft copolymers, which locate themselves preferentially at the interface of polymer blends. As a result, they tend to reduce the interfacial tension, strengthen the interfacial adhesion and prevent coalescence of dispersed phase^[12, 13]. Tang and Becker^[14, 15] studied the effect of a compatibilizer on the morphology and mechanical properties of polypropylene (PP)/thermoplastic polyurethane (TPU) blends and amorphous polyamide (aPA)/acrylonitrilestyrene copolymer (SAN) blends. They found that the dispersion of TPU and SAN phase and the tensile modulus of the blends were remarkably improved after compatibilization. A better adhesion between PET and iPP with the compatibilization of silane coupling agents was also observed by Oyman *et al.*^[16], resulting in improvement of tensile strength and impact strength. However, it is difficult and high-cost to design and synthesize a particular compatibilizer separately for a particular pair of immiscible polymers at an industrial scale^[17], whereafter increasing efforts have been made towards *in situ* reactive compatibilization of immiscible polymer blends by reactive extrusion^[18, 19], which can be classified as one-step and two-step reactive extrusion. Compared with two-step reactive extrusion, one-step reactive extrusion is more efficient and more economical^[20]. Hu *et al.* successfully achieved *in situ* compatibilization of polypropylene/poly(butylene terephthalate) blend and polyethylene/polyamide 6 blend with improved mechanical properties, which demonstrated the feasibility and advantages of one-step reactive extrusion^[21]. Furthermore, we have documented that PET microfibrils could also form, when compatibilizers (such as ethylene vinyl acetate copolymer (EVA), propylene-glycidyl methacrylate (PP-GMA)) were added into the microfibrillar blends^[22, 23]. For this blend, the tensile and izod impact strength increased with the optimum amount of compatibilizer (about 2 wt%), at the same time, the tensile modulus and flexural modulus almost kept unchanged^[23]. Therefore, in this paper, we applied one step *in situ* compatibilization to the microfibrillation of iPP/PET blends, hoping achievement of both fibril-like dispersed phase and good interface adhesion conveniently.

It has been well known that the crystalline morphology of iPP matrix in microfibrillar blends formed during processing will determine mechanical properties directly^[10]. In our previous study^[24], for microfibrillar reinforced iPP/PET blends, the crystallization rate of iPP increased distinctly and its transcrystallinity formed in vicinity of PET microfibrils due to its high heterogeneous nucleation. Subsequently, we reported that more homogeneous crystal orientation appeared in the corresponding injection molded parts with presence of PET microfibrils network, leading to better mechanical properties^[25]. For compatibilized microfibrillar reinforced iPP/PET blends, the compatibilizer affects the morphology of PET microfibril and tends to stay on the interface between fibril phase and matrix^[23], therefore, crystallization behavior and morphology could be different from un-compatibilized microfibrillar reinforced iPP/PET blends we studied previously. Furthermore, studying non-isothermal crystallization behavior of microfibrillar reinforced iPP/PET blends with compatibilization will provide a guideline to design the processing parameters and clarify the relationship between morphology of dispersed phase and crystallization behavior of iPP/PET blends, and subsequently control their mechanical properties.

In present work, we applied one-step reactive compatibilization and microfibrillation technology to prepare one-step reaction compatibilized microfibrillar reinforced *i*PP/PET blends (CMRB). The morphology and crystallization behavior of CMRB were studied by using scanning electron microscope (SEM), differential scanning calorimeter (DSC), and polarized optical microscope (POM). Two-dimensional wide angle X-ray diffraction (2D-WAXD) was also employed to investigate the crystal modifications of *i*PP during molding injection. The aim is to reveal the effect of *in situ* compatibilization on morphology and crystallization of microfibrillar reinforced *i*PP/PET blends, and to obtain improved mechanical properties of microfibrillar reinforced polymer blends through controlling morphology of dispersed phase and interfacial adhesion between matrix and dispersed phase during practical processing in further study.

EXPERIMENTAL

Materials

*i*PP, (T30S), was purchased from Dushanzi Petroleum Chemical Co. (China) with M_w of *ca.* 39.9×10^4 , $M_w/M_n = 4.6$ and melt flow rate (MFR) of 3 g/10min (230°C, 21.6 N). PET with M_n of *ca.* 11.0×10^4 was supplied in pellets by Luoyang Petroleum Chemical Co. (China). Glycidyl methacrylate (GMA, 97% purity), styrene (STY, 99% purity) and dicumyl peroxide (DCP) were purchased from Aldrich. Dicumyl peroxide (DCP) was used as free radical initiator. Styrene was used to assist the free radical grafting of GMA. All the agents were used without further purification. In order to avoid hydrolysis, PET was dried in a vacuum oven at 120°C for at least 10 h before processing.

Preparation of One-step Reaction Compatibilized Microfibrillar Reinforced *i*PP/PET Blends (CMRB)

The GMA and DCP were mixed with *i*PP using a fixed composition *i*PP/GMA/DCP = 100/0.5/0.15 (*W/W/W*), mole ratio of styrene and GMA was set at 0.5 and the dried PET pellets were dry-mixed with *i*PP pellets at a constant mass ratio of 80/20 (*i*PP/PET). Subsequently, the mixture was fed into an extruder, and the compatibilized microfibrillar reinforced *i*PP/PET blend was prepared through the “extrusion-hot stretching-quenching” process under the processing temperature of PET (*ca.* 270°C)^[22]. Extrusion of the mixture was performed on a single-screw extruder having a screw length to screw diameter, L/D , of 30, and the die for the extruder was a slit die with 20 mm width and 1 mm thickness. The temperature profile from hopper to die of the extruder was 160°C, 270°C, 275°C and 270°C, respectively, and the screw rotation was maintained at 65 r/min. The extrudate was hot stretched by a take-up device with three pinching rolls to form PET microfibrils, and the roll temperature was kept at about 40°C by adjusting the volume flow rate of tap water in cooling pipe. Although different hot stretching ratios (HSRs, the ratio of the transverse section of the die to the transverse section of the extrudate) could be obtained by changing the speed of the take-up device, HSRs was maintained at 18 in this study. Subsequently, the stretched extrudate was immediately quenched in a cold water bath after stretching and thin ribbon with a thickness of about 0.2 mm was obtained and pelletized. Detailed preparation process can refer to the paper of Li *et al.*'s work^[24]. For comparison, compatibilized *i*PP/PET common blend (CCB) was obtained without hot-stretching (*i.e.* as-extruded blend). In addition, microfibrillar reinforced *i*PP/PET blend (MRB) without *in situ* compatibilized agents (*i.e.* GMA, DCP, and St) was prepared by using the same processing condition of CMRB. Injection molding was conducted for the three pelletized materials (MRB, CMRB and neat *i*PP) after they were dried in a vacuum oven at 120°C for 5 h. The temperature was set at 165°C, 205°C, 210°C, 205°C from hopper to nozzle, respectively, far below the melting point of PET (around 255°C), in order to keep PET microfibrillar morphology.

Fourier Transform Infrared (FTIR) Spectroscopy

To depict the chemical reaction between terminal groups (—OH and —COOH) of PET and maleic anhydride or epoxy groups of GMA grafted polypropylene, FTIR characterization was performed on a Nicolet-560 FTIR spectrometer (Nicolet Corp., USA), the resolution was 2 cm^{-1} . Thin films for FTIR characterization were prepared on a hot stage at 270°C using the as-fabricated specimens.

Scanning Electronic Microscopy (SEM)

For phase morphology observation, the matrix iPP in the specimens was selectively dissolved by immersing it into a hot xylene at 110°C for 1 h. After the solvent volatilized completely, the surfaces were coated with a layer of gold and the domain morphology was observed by using a JEOL JSM-5900LV scanning electron microscope (SEM). Additionally, for CCB sample, the cryo-fracture surface was used for SEM observation.

Differential Scanning Calorimetry (DSC)

DSC studies were performed on a TA-DSC 910s. To characterize the crystallization process, detailed procedure was set as follows: (a) the samples mentioned above (5–10 mg) were heated up to 200°C at a constant heating rate of 10 K/min under nitrogen atmosphere and kept at this temperature for 5 min to eliminate any thermal and mechanical history; (b) cooled each sample at a cooling rates of 2.5 K/min; (c) the data from 40°C to 200°C were collected with the help of a Star system. To investigate the melting behavior, the samples were heated to 200°C with the heating rate of 10 K/min.

Polarized Optical Microscopy (POM)

A Leica DMIP POM equipped with a Linkam THMS 600 hot stage was used to measure the crystalline morphology evolution of these samples. Samples were melted and squeezed between microscopic glass slides at 200°C for 5 min, whereafter samples were cooled to room temperature at 2.5 K/min. In practical examination, the crystalline morphologies for the undiluted PET/iPP blends are hard to identify. Hence, PET/iPP blends were mixed with some fresh neat iPP resin at 200°C in a Haake rheometer to be diluted to 1 wt% PET concentration. The phase morphologies of PET in PET/iPP blends can be maintained under such mixing temperature which is much lower than the melting temperature of PET.

Two-dimensional Wide-angle X-ray Diffraction (2D-WAXD)

To characterize crystalline structure morphology of the samples in actual processing by using the 2D-WAXD, we started with a 6.0 mm wide and 4.0 mm thick dumbbell tensile bar and machined away all of the tensile bar except for a 1.0 mm thick piece (the 6.0 mm width remains unchanged), detailed preparation information can refer to Chen *et al.*'s work^[26]. The direction normal to MD-TD (the molding direction-transverse direction) plane was defined as ND (normal direction). The X-ray beam was perpendicular to MD-ND plane and scanned the intermediate layer (0.5–1.0 mm down from the MD-TD surface). The measurements were performed in transmission geometry on the synchrotron light source (wavelength $\lambda = 0.14809$ nm) with the MarCCD as detector at National Synchrotron Radiation Laboratory, China.

1D-WAXD curves were obtained from circularly integrated intensities of 2D-WAXD image patterns for revealing crystal modifications clearly. For evaluation of molecular orientation, the Hermans orientation parameter was used, which defined as

$$\langle P_2(\cos\phi) \rangle = (3\langle \cos^2\phi \rangle - 1)/2 \quad (1)$$

where $\langle \cos^2\phi \rangle$ is an orientation factor defined as

$$\langle \cos^2\phi \rangle = \int_0^{\pi/2} I(\phi) \cos^2\phi \sin\phi d\phi / \int_0^{\pi/2} I(\phi) \sin\phi d\phi \quad (2)$$

where $I(\phi)$ is the scattering intensity at ϕ . The orientation parameter was calculated mathematically using Picken's method from the (040) azimuthal distribution of PP obtained from the 2D-WAXD patterns^[27].

RESULTS

In situ Compatibilization Reaction Characterized by FTIR

As shown in Fig. 1 (curve b), the absorption bands of epoxy group (C—O—C) in PP-g-GMA are located at 1221 cm⁻¹ and 1166 cm⁻¹^[28]. For one-step reaction compatibilized iPP/PET blend (curve d in Fig. 1), the

intensity of those bands decreases sharply, indicating the reaction between epoxy groups of PP-g-GMA and terminal groups ($-\text{OH}$ and $-\text{COOH}$) of PET^[29–32]. Furthermore, in our previous work^[23], two-step reactive extrusion was employed to prepare compatibilized *i*PP/PET microfibrillar reinforced blends, distinct compatibilization was observed and PET domains decreased. Comparing FTIR spectra of the one-step reaction compatibilized *i*PP/PET blends (curve d) with those of two-step extrusion products (curve c), one could find that the two spectra almost overlap each other, indicating that same products were prepared through the above two processes. From Hu's work^[33], one could see that the process of free radical grafting of GMA onto PP is easy to occur with the aid of styrene monomer. Thus we can conclude that the successful and desired products were obtained through the one-step reactive extrusion, although just indirect evidence is presented in this paper.

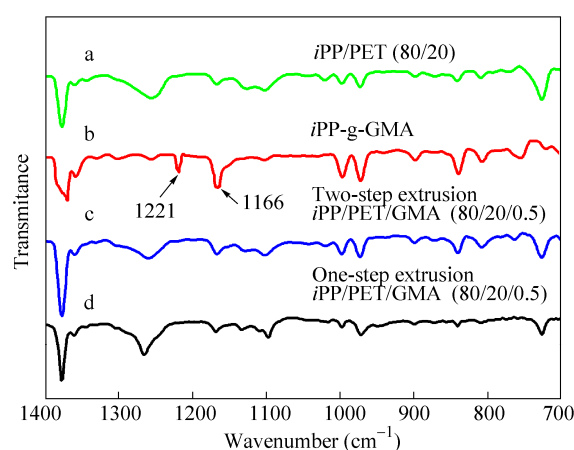


Fig. 1 FTIR spectra of compatibilized *i*PP/PET blends

Morphology of PET Dispersed Phase Characterized by SEM

The morphologies of CCB, MRB and CMRB are shown in Fig. 2. In the CCB, PET phase in the form of spherical and elliptical particles with their edges fused with *i*PP matrix is found, in other words, no sharp-edged morphology of interphase between PET and *i*PP phases can be found from the SEM images of cryo-fracture surface of CCB, which is attributed to the improved interfacial compatibility. Moreover, one could observe that PET particles exhibit uniform dispersion in *i*PP matrix. The samples of CMRB and MRB etched by hot xylene show microfibrillar morphology of the PET phase and large bunches of PET microfibrils are observed in the micrographs. Compared to CMRB, the PET microfibrils in the MRB are more uniform. Although the measurement of the aspect ratio is unattainable as it is difficult to observe intact microfibrils, the SEM images clearly indicate compatibilization before stretching is not conducive to form fine microfibrils. The observations are similar to what we found when the compatibilizer PP-g-GMA was added *ex-situ* during fabrication of microfibrillar reinforced *i*PP/PET blend, and the phenomenon was ascribed to the increase of viscosity ratio and preventing coalescence with the presence of compatibilizer.

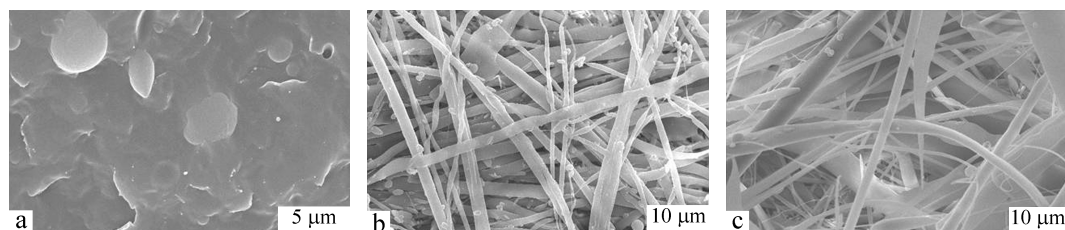


Fig. 2 SEM micrographs of (a) CCB (cryo-fracture surface in liquid nitrogen), (b) MRB and (c) CMRB (surface etched by hot xylene)

Non-isothermal Crystallization Characterized by DSC

The crystallization exotherms of neat iPP, CCB, MRB and CMRB at cooling rate of 2.5 K/min are presented in Fig. 3. Actually, we obtained DSC curves at cooling rates of 2.5, 5, 10 and 20 K/min and all of them exhibited the same tendency, therefore, DSC curves at cooling rate of 2.5 K/min were selected as a representation. On the basis of these curves at cooling rate of 2.5 K/min, one can easily conclude that for samples containing PET phase, the onset and maximum crystallization temperatures are higher than those of neat iPP, respectively. Furthermore, combination of the DSC curves with the above SEM images clearly indicates that crystallization onset (and peak) temperature increases with the uniformity of PET microfibrils. This phenomenon illustrates that well-defined PET microfibrils are favorable to the iPP crystallization in iPP/PET blends.

Figure 4 plots relative crystallinity ($X(T)$) as a function of crystallization time (t) for neat iPP, CCB, MRB and CMRB at a cooling rate of 2.5 K/min.

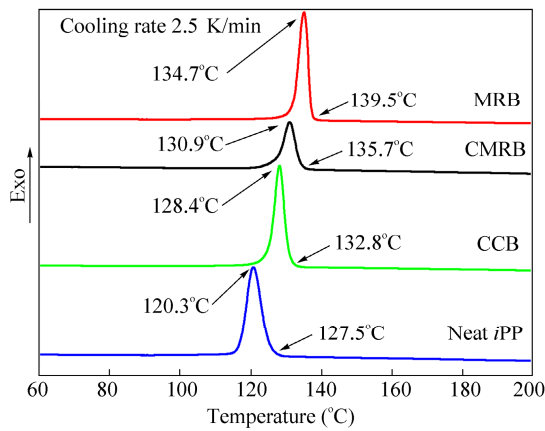


Fig. 3 Nonisothermal crystallization curves of neat iPP, CCB, MRB and CMRB at the cooling rate of 2.5 K/min

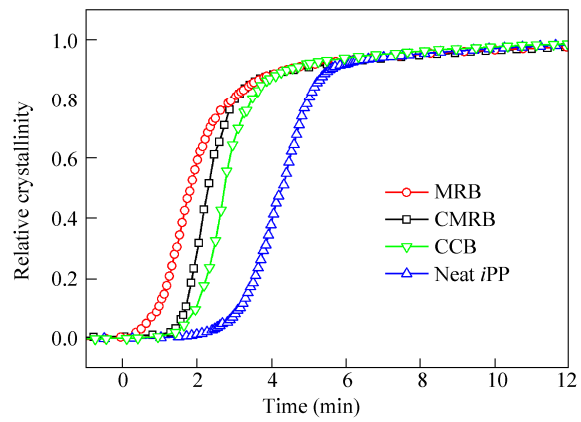


Fig. 4 Plots of $X(T)$ versus T for neat iPP, CCB, CMRB and MRB at cooling rates of 2.5 K/min

The relative crystallinity, $X(T)$, is calculated by Eq. (3)

$$X(T) = \frac{\int_{T_0}^T \left(\frac{dH}{dt} \right) dt}{\int_{T_0}^{T_2} \left(\frac{dH}{dt} \right) dt} \times 100\% \quad (3)$$

where T_0 and T_2 are the onset and end of crystallization temperatures, respectively, and dH/dt is the heat-evolution rate. $X(T)$ - T curve is achieved by this way. Then, using $t = (T_0 - T)/R$ (where T is the temperature at crystallization time t , R is the cooling rate), the abscissa of temperature can be transformed into a time scale to attain Fig. 4.

These curves illustrate that at the same crystallization time, samples containing PET phase have higher relative crystallinity than neat iPP, and MRB owns the highest relative crystallinity among the four samples, followed by CMRB and CCB, respectively. On the basis of these results, it is concluded that the MRB has the highest crystallization rate, followed by the CMRB and the CCB in order, and the neat iPP crystallized with the lowest crystallization rate. The DSC curves (Fig. 4) illustrate that morphology of PET microfibrils plays an important role in enhancing crystallization rate. In other words, the PET domains in iPP matrix act as heterogeneous nuclei during the nonisothermal crystallization process; hence, the crystallization rate of the iPP phase increased. When the PET pellets were deformed into microfibrils during processing, their effects on iPP crystallization are enhanced more obviously.

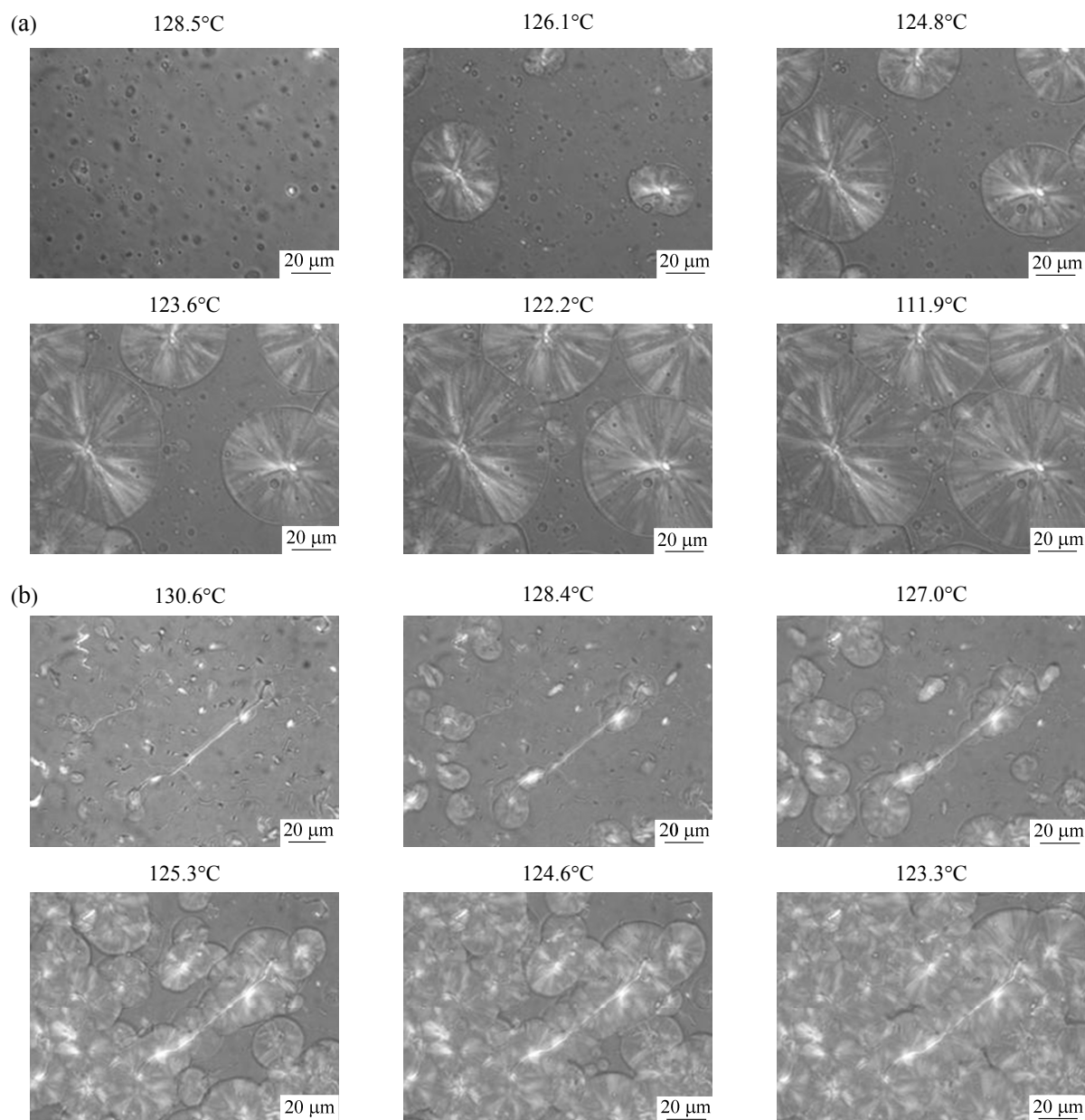


Fig. 5 Polarized optical micrographs of CCB (a) and CMRB (b) crystallized nonisothermally at cooling rate of 2.5 K/min

Crystalline Morphology Evolution Characterized by POM

Figure 5 depicts the polarized optical micrographs of CMRB and CCB crystallized nonisothermally at a cooling rate of 2.5 K/min. As for the CCB, the growth of typical spherulites is observed during nonisothermal crystallization, one can clearly observe that the PET particles act as nuclei for heterogeneous nucleation of the *i*PP spherulites, but for the CMRB, more nuclei appear since average size of final spherulites decreases, moreover, nucleation on surface of PET microfibrils can be observed clearly, indicating stronger heterogeneous nucleation ability of PET microfibrils. Therefore, combination of the DSC and the POM results indicates that the onset temperature of nonisothermal crystallization of *i*PP can be enhanced by adding PET particles or PET microfibrils due to their heterogeneous nucleation ability. For the MRB and the CMRB, the higher

crystallization rate of MRB can be ascribed to narrower and more uniform distribution of PET microfibrillar diameter; meanwhile, for the CMRB and the CCB, the difference of their crystallization rate could result from stronger heterogeneous nucleation ability of PET microfibrils compared to PET particles.

The Crystalline Structure and Orientation Characterized by 2D-WAXD and DSC

Figure 6 shows the selected 2D-WAXD patterns of the four samples from the intermediate layer of injection molded parts. The 2D-WAXD patterns of the neat iPP and the CCB show five diffraction rings associated with different lattice planes of iPP, from inner to outer circles, corresponding to (110), (040), (130), (111) and (131) crystal planes^[34], respectively, which are characteristic of α -phase crystals. For the MRB sample and the CMRB sample, two additional diffraction rings exist in the 2D-WAXD patterns, which correspond to the (300) and (311) crystal planes of β -form crystals. It can be seen more vividly in Fig. 7 that the (300) reflection of β -form crystals does exist in the intermediate lay of the MRB sample and the CMRB sample but is absent in the neat iPP sample and the CCB sample, moreover, the intensity of the (300) reflection in the MRB sample is higher than that of the CMRB sample, which indicates that β -form crystals can develop more easily in the MRB sample in actual processing due to existence of finer microfibrils formed in the MRB samples.

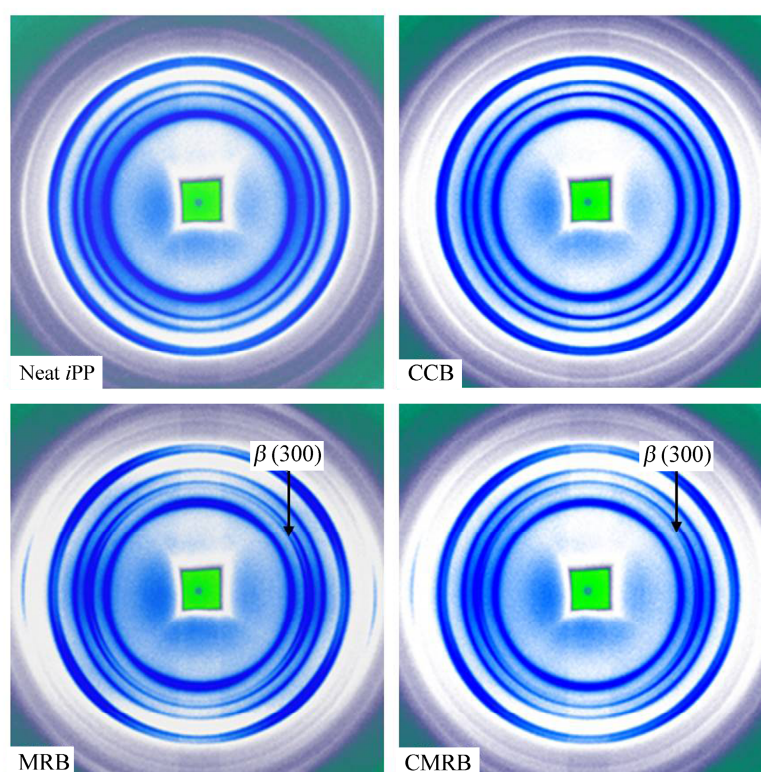


Fig. 6 2D-WAXD patterns of neat iPP, CCB, MRB and CMRB

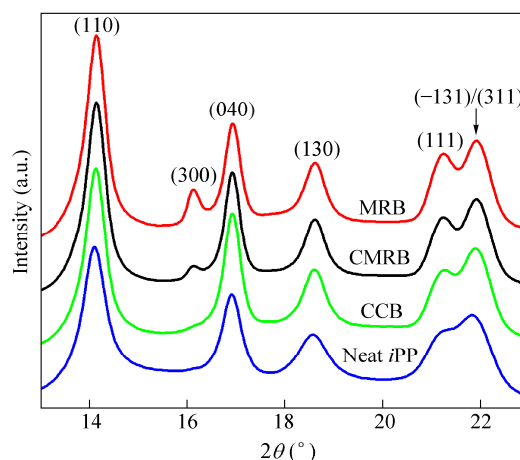


Fig. 7 1D-WAXD curves obtained from circularly integrated intensities of 2D-WAXD patterns in Fig. 6

The degree of crystal orientation responsible for strength is the highest for MRB, followed by CMRB; for neat *i*PP and CCB, the orientation parameters are much lower and the difference (*i.e.*, 0.02) between them is almost negligible (Fig. 8 and Table 1). In the microfibrillar blends (MRB and CMRB), the orientation parameters (*ca.* 0.607, 0.757) are almost identically high, which indicates that PET microfibrils formed in *i*PP/PET blends are favorable for molecular orientation in actual processing.

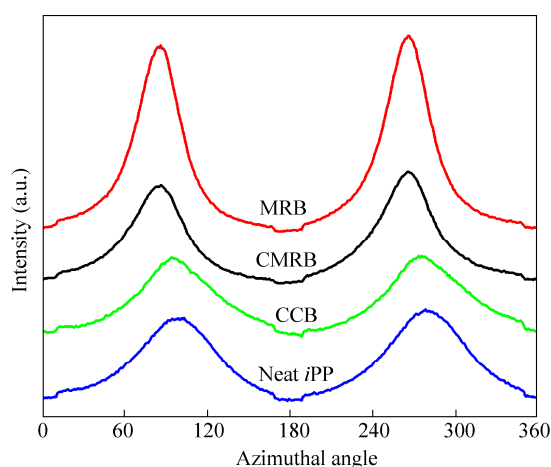


Fig. 8 Intensity distribution of $\alpha(040)$ along azimuthal angle calculated from 2D-WAXD patterns

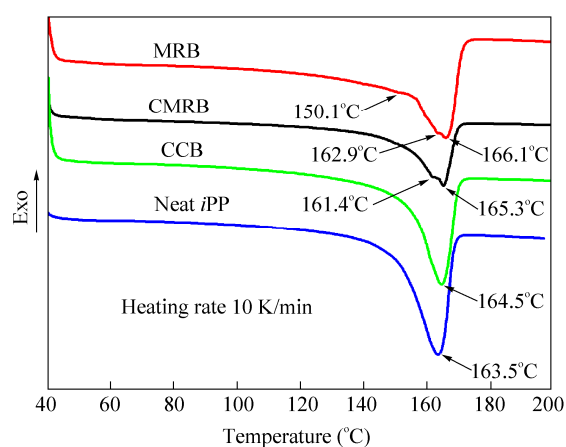


Fig. 9 DSC heating curves of neat *i*PP, CCB, MRB and CMRB

Table 1. Degree of crystal orientation fitted from the intensity of $\alpha(040)$ along azimuthal angle

Neat <i>i</i> PP	CCB	CMRB	MRB
0.301	0.321	0.607	0.757

Figure 9 shows DSC heating curves of the four samples. For the neat *i*PP sample and the CCB sample, the intermediate layers of injection molded parts show a single melting behavior, which represents the melting of α -phase of *i*PP. In contrast, the intermediate layers of injection molded parts of the MRB sample and the CMRB sample show two endothermic peaks of α -phase, corresponding to α -form lamellar crystals and stretched α -

crystals (shish crystal), respectively. Moreover, in the intermediate layer of the MRB sample, an obvious endothermic peak appears at the temperature of around 150.1°C which is attributed to melting of β -phase of iPP^[35, 36]. In summary, the melting temperature of samples containing PET microfibrillar phase is higher than that of the neat iPP sample and the CCB, indicating that the heterogeneous nucleation of PET microfibrils accelerates the crystallization and improves the perfection of crystals in the actual processing.

DISCUSSION

The Effect of in situ Compatibilization on Morphology of PET Microfibrils

A desirable and stabilized morphology of an immiscible polymer blend with strong interfacial compatibility often requires the presence of an appropriate compatibilizer^[17]. In this work, compatibilizer was generated in a simple way, one-step reactive extrusion, to achieve improved interfacial compatibility between PET dispersed phase and iPP matrix (see Fig. 2). We also found out that, for microfibrillar reinforced iPP/PET blends, the morphology of PET microfibrils was deteriorated with *in situ* compatibilization, *i.e.* leading to thicker microfibrils with broader distribution. Scott and Macosko^[37, 38] have proved that the formation of *in situ* microfibrillation includes two synchronous processes: the large deformation of dispersed phase droplets and the coalescence of deformed droplets during stretching. According to the process of microfibrils' formation, one can easily understand that the size of droplets and their distribution dominate the corresponding morphology of microfibrils and their distribution. Also, we should bear in mind that PET particles' size depends on the combined effect of the decrease of surface tension and increase of viscosity ratio of PET melt to iPP melt^[39]. As our previous work^[23] presented, compatibilization can increase viscosity ratio and decrease interfacial tension between PET and iPP, which tends to decrease the size of PET phase droplets in the non-stretched blends. Therefore, this means smaller PET particles existing in the compatibilized blends than in uncompatibilized ones based on above analysis. Additionally, in the CMRB the reaction of functional groups between PP-g-GMA and PET enhances the contact of the interfaces, and viscosity ratio of PET phase to iPP matrix increases, which hampers the microfibrillation process of PET phase, due to the presence of resistance when stretching is imposed on the compatibilized blends. After stretching, the aspect ratio of PET microfibrils in the compatibilized blends is considerably reduced compared to the uncompatibilized ones. On the other hand, besides the viscosity ratio effect, the coalescence of deformed droplets, which also determines microfibrils' morphology, is affected by the *in situ* compatibilizer. In the CMRB, the *in situ* compatibilizer locating in interphase between PET phase and iPP matrix prevents deformed PET domains from coalescing each other during drawing and from forming microfibrils with large aspect ratios.

The Crystallization and Crystalline Modifications in CMRB

For crystallization behavior of microfibrillar blends, it is well known that crystallization usually includes two processes: formation of nucleus and growth of crystal, which determine the whole crystallization rate. The PET phase could act as heterogeneous nuclei for iPP crystallization, leading to increase of crystallization temperature^[40, 41]. Based on our previous work, morphology of PET dispersed phase, such as its diameter and aspect ratio, also plays an important role in the crystallization behavior of the iPP/PET blends^[24, 42]. The existence of PET microfibrillar phase can enhance crystallization temperature of iPP with onset temperature higher than that of iPP/PET common blends under quiescent condition due to larger effective surface of microfibrils for nucleation^[24], which is why the crystallization temperature of the CMRB sample is higher than that of the CCB sample. Furthermore, compared with the MRB sample, the CMRB sample has lower crystallization temperature due to the existence of PET microfibrils with smaller aspect ratio and wider distribution. In addition, since *in situ* compatibilizer tends to stay in the interphase^[23], it could also hinder the diffusion of iPP molecules to the surface of PET phase, leading to decrease of crystallization rate.

The results of 2D-WAXD and DSC melting curves indicate that β -form iPP crystals were generated in stretched iPP/PET blends through actual processing, and in the CMRB samples, the content of β -form iPP was lower than that of the MRB samples. In other words, well-developed microfibrils promote the formation of β -

form *i*PP in actual processing. It is found that β -form *i*PP can be obtained through several methods, such as addition of β nucleating agents^[43–45], crystallization in a temperature gradient^[46] and shear-induced β -form *i*PP^[47]. In our case, the spherical PET phase cannot induce β -form *i*PP (see Fig. 7). Furthermore, in our previous study, it was found that row nuclei, which was the prerequisite of formation of shear induced β -form *i*PP, can be induced both by simply shear stress and by microfibril under shear flow^[42], *i.e.* local shear stress near the surfaces of PET microfibrils due to severe relative flow during melt flow could be favorable for formation of row nuclei. Therefore, we can deduce that β -form *i*PP existing in MRB and CMRB samples is induced by the combination effect of PET microfibrils and shear stress. As for the CMRB, the microfibrils tend to become short and non-uniform, which could weaken the local shear stress and lead to low content of β -form *i*PP.

CONCLUSIONS

One-step reactive compatibilization was successfully applied to the microfibrillation of *i*PP/PET blends. The compatibilized common blend (CCB), in which the PET phase presented typical spherical domain, has a partial compatible blend morphology comprising discrete domains of the minor phase dispersed in a continuous phase of major component and shows improved interfacial compatibility. The PET microfibrils were generated *in situ* during “slit extrusion-hot stretching-quenching” process, although those microfibrils had relatively small aspect ratio and wide distribution compared to microfibrillar reinforced *i*PP/PET blend without compatibilization. Both spherical PET phase and microfibrillar phase can serve as the nucleating agents to increase crystallization temperature and overall crystallization rate of *i*PP during the nonisothermal crystallization process. Moreover, PET microfibrils present stronger heterogeneous nucleation ability than spherical PET phase. An interesting observation is that well-developed PET microfibrils existing in *i*PP/PET blends promote the formation of β -phase crystals of *i*PP in actual processing. The microfibrils with large aspect ratio and narrow diameter distribution can yield a high heterogeneous nucleation ability and high content of β -crystal.

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